
Standard Operating Procedure for Analysis of Ink *and coating* Samples by Reference Methods 24 and 24A

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**STANDARD OPERATING PROCEDURE FOR
ANALYSIS OF COATING AND INK SAMPLES
BY REFERENCE METHODS 24 AND 24A**

**U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning and Standards
Stationary Source Compliance Division
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SECTION 1

INTRODUCTION

This standard operating procedure document is prepared with the intent of providing simple step-by-step instructions, covering all aspects of laboratory handling and analysis of coating and ink samples, for use by EPA, State, and local regulatory agency laboratories as well as contract laboratories nationwide. The instructions are presented in general terms as much as possible while providing sufficient details for accurate and precise laboratory measurements to be done. The procedures should be used in conjunction with existing health and safety programs and in accordance with existing EPA or other agency training guidelines.

Standard procedures are presented in this report for the handling and physical/chemical characterization of coating and ink samples that require analysis by EPA Reference Methods 24 or 24A (RM 24/24A) as found in 40 CFR 60, Appendix A. This document has been expanded from an original version obtained from the Wisconsin Occupational Health Department covering laboratory determinations of the VOC content, water content, and density of coating and ink samples taken for environmental compliance. For the purpose of developing consistency among analytical laboratories nationwide, it delineates the activities deemed proper and necessary to ensure that an accurate and precise measurement of coating or ink sample properties are made. If the activities are conducted as described, questions concerning the validity and reproducibility of analyses performed can be avoided.

The purpose of these standard operating procedures (SOPs) for RM 24 and RM 24A is to ensure that laboratory analyses are performed in such a way that review, interpretation, and use of the laboratory analysis results by EPA, State, and local regulatory agency personnel is facilitated.

The procedures cover all types of industrial coating and printing ink operations, regardless of the method of application of coating or ink, including, for example, dip, spray, roll, flow, electrostatic, or electro-deposition processes. Special cases involving use of exempt solvents dichloromethane (methylene chloride) and 1,1,1-trichloroethane (methyl chloroform) or multi-component mixture coating formulations are covered in accordance with most recent technical and regulatory thinking, however, this is not a regulatory but a technical procedure guideline document.

In addition to the introduction given here, Section 2 of this document contains a summary of sample handling procedures to be followed; Section 3 contains EPA Reference Method 24 including draft revision amendments which are being considered to make it applicable to multi-component coatings and exempt solvents; Section 4 contains detailed SOPs for EPA Method 24 analyses for percent water content,

percent volatile content, exempt solvent (dichloromethane and 1,1,1-trichloroethane), and density of coatings; Section 5 contains EPA Reference Method 24A for determination of volatile matter and density of printing inks; Section 6 contains SOP guidance for EPA Method 24A analyses; and Section 7 contains a detailed bibliography of documents relevant to EPA Method 24/24A analyses.

SECTION 2

SAMPLE HANDLING PROCEDURES

There are several steps to be taken at the laboratory upon receipt of a sample for analysis according to EPA Reference Methods 24 and 24A. These are outlined below:

1. Inspect the shipping package for damage and proper labeling. If improper labeling, delayed shipping, damage, spillage, or other problem is evident, notify the sending agency by phone as soon as possible.
2. Open the shipping package and record in a laboratory notebook or recordbook relevant observations and information from containers, labels, shipping papers, Material Safety Data Sheets (MSDS) forms, and Chain of Custody (C of C) documents, which should be enclosed with the samples. Include the following:
 - 2.1 Name of person who collected the samples, the date/time the samples were obtained, and the date/time the samples were shipped to the laboratory for analysis.
 - 2.2 Name, phone number, and address of agency and person to whom results of analyses are reported.
 - 2.3 Facility or source identification to be coded or numbered.
 - 2.4 Sample identification number and a brief description of the sample and container.
 - 2.5 Analyses required, RM 24, RM 24A, multi-component, or exempt solvent determinations.
 - 2.6 Describe the physical appearance of the sample on first opening (e.g., full to top, not tightly sealed or inner seal missing, appearance (color), type of ink/coating, odor, or presence of residue).
 - 2.7 Summarize MSDS information, if available, for safety and handling purposes.

- 2.8 If special multi-component sample blending or exempt solvent determination is required, contact sending agency personnel for instructions on set-up (hardening) time and mixing proportions.
 - 2.9 Report problems with sampling integrity or inconsistencies in documentation, including missing (or occasionally too much) information on the labels or C of C forms.
 - 2.10 Start any internal laboratory sample recordkeeping procedures normally used to track samples.
- 3. After signing the C of C receipt of the samples, send the original of the C of C documents back to the appropriate sending agency personnel for their records and keep a copy for laboratory records.
 - 4. Secure the samples with a copy of the C of C documents and MSDS forms in a locked storage cabinet dedicated to environmental samples. If this is done by a sample custodian designated to retain custody of the sampling pending analysis, then that person should sign the C of C forms acknowledging receipt of the samples. Maintain samples at room temperature, preferably at 70°F but within the range of 40 to 100°F.

During and at the end of sample analyses, there are several steps to be taken related to disposal of waste materials from the sample and the laboratory analysis. These are summarized below:

- 5. A plastic bag should be used to discard waste ink solids, rags, paper towels, kimwipes, and other non-glass or non-sharp items. This can normally be disposed of with industrial solid waste material.
- 6. A separate container (e.g., a glass bottle or metal/plastic can), should be used for collection and eventual disposal of discarded glassware and other sharp-edged items used in the laboratory. This may be discarded with industrial solid waste, but must be given careful handling during disposal.
- 7. A 5-gallon solvent-resistant plastic or metal container with a lid or cover designed for flammable liquids should be stored in the hood where analytical work is performed. It should be used to collect unused or excess sample, reagents, and mixtures of both for periodic disposal as a liquid waste. Fiber mesh material can be used to filter out solids from liquid wastes that are deposited into the container. A list of compounds which are placed in the container should be kept as a record for

identification of the contents upon disposal. Liquid waste should be sent out for disposal to a reputable disposal organization.

8. After analyses are completed (or approximately 30 days), the samples in their sample containers should be attached to their MSDS forms identifying the approximate composition, physical and chemical properties, and safety hazards associated with the sample. They should then be sent out for disposal to a reputable disposal organization. If analyses have not been completed within 30 days, it is recommended that another sample should be taken since the chemical/physical composition of the existing sample may have changed significantly over the time period.

SECTION 3

REFERENCE METHOD 24—DETERMINATION OF VOLATILE MATTER CONTENT AND DENSITY OF PRINTING INKS AND RELATED COATINGS

EPA Reference Method 24 as it appears in 40 CFR Part 60, Appendix A (7-1-90 edition) is presented here, starting on the following page, with draft revisions under consideration by EPA shown in bold italics. These revisions incorporate procedures to be used with multi-component coatings and exempt solvents which are not addressed in the 7-1-90 edition of 40 CFR 60, Appendix A.

Analysis for exempt solvents in coatings is practiced according to ASTM D4457-85 - "Standard Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph." In the draft revisions to EPA Method 24, this procedure is incorporated by reference.

Proposed guidance for handling multi-component coatings, developed for incorporation into EPA Method 24, includes revisions to the existing text and some additional text. In the revisions, existing Sections 3.1, 3.2, 3.3, and 3.4 have been redesignated as Sections 3.2, 3.3, 3.4, and 3.5, respectively; Sections 5.1 and 5.2 have been revised; and new Sections 2.5, 3.1, 3.6, and 3.7 have been added, as shown in bold italics on the following pages.

**REFERENCE METHOD 24 - DETERMINATION OF VOLATILE MATTER CONTENT,
WATER CONTENT, DENSITY, VOLUME SOLIDS, AND WEIGHT SOLIDS OF SURFACE
COATINGS**

40 CFR Part 60, Appendix A
(7-1-90 Edition)
Final, promulgated 10/3/80
45 FR 65958

Current Draft Revisions Shown in Bold Italics

1. Applicability and Principle

- 1.1 Applicability. This method applies to the determination of volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or related surface coatings.
- 1.2 Principle. Standard methods are used to determine the volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or related surface coatings.

2. Applicable Standard Methods

Use the apparatus, reagents, and procedures specified in the standard methods below:

- 2.1 ASTM D1475-60 (Reapproved 1980), Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products (incorporated by reference--see §60.17).
- 2.2 ASTM D2369-81, Standard Test Method for Volatile Content of Coatings (incorporated by reference--see §60.17).
- 2.3 ASTM D3792-79, Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection into a Gas Chromatograph (incorporated by reference--see §60.17).
- 2.4 ASTM D4017-81, Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Titration Method (incorporated by reference--see §60.17).
- 2.5 ***ASTM D4457-85 Standard Test Method for Determination of Dichloromethane and 1,1,1-Trichloromethane in Paints and Coatings by Direct Injection into a Gas Chromatography.***

3. Procedure

3.1 Multi-Component Coatings. *To determine the total volatile content, water content, and density of multi-component coatings, follow the procedures in Section 3.7. Multi-component coatings are coatings that are packaged in two or more parts, which are combined before application. Upon combination a coreactant from one part of the coating chemically reacts, at ambient conditions, with a coreactant from another part of the coating. For all other coatings analyze as follows:*

3.2 Volatile Matter Content. Use the procedure in ASTM D2369-81 (incorporated by reference--see §60.17) to determine the volatile matter content (may include water) of the coating. Record the following information:

W_1 = Weight of dish and sample before heating, g.

W_2 = Weight of dish and sample after heating, g.

W_3 = Sample weight, g.

Run analyses in pairs (duplicate sets) for each coating until the criterion in Section 4.3 is met. Calculate the weight fraction of the volatile matter (W_v) for each analysis as follows:

$$W_v = \frac{W_1 - W_2}{W_3} \quad \text{Eq. 24-1}$$

Record the arithmetic average ($\overline{W_v}$).

3.3 Water Content. For waterborne (water reducible) coatings only, determine the weight fraction of water (W_w) using either "Standard Content Method Test for Water of Water-Reducible Paints by Direct Injection into a Gas Chromatograph" or "Standard Test Method for Water in Paint and Paint materials by Karl Fischer Method." (These two methods are incorporated by reference - see §60.17.) A waterborne coating is any coating which contains more than 5 percent water by weight in its volatile fraction. Run duplicate sets of determinations until the criterion in Section 4.3 is met.

Record the arithmetic average ($\overline{W_w}$).

- 3.4 Coating Density. Determine the density (D_c , kg/liter) of the surface coating using the procedure in ASTM D1475-60 (Reapproved 1980) (incorporated by reference - see §60.17). Run duplicate sets of determinations for each coating until the criterion in Section 4.3 is met.

Record the arithmetic average ($\overline{D_c}$).

- 3.5 Solids Content. Determine the volume fraction (V_s) solids of the coating by calculation using the manufacturer's formulation.

- 3.6 *Exempt Solvent Content. Determine the weight content of exempt solvents (W_e) by using ASTM Method D4457-85 (incorporated by reference - see § 60.17). Run a duplicate set of determinations.*

Record the arithmetic average ($\overline{W_e}$).

Note: exempt solvents are defined as those solvents listed in 57 FR 3941, February 3, 1992. Dichloromethane and 1,1,1-trichloroethane are listed exempt solvents and may be used in coatings.

- 3.7 To determine the total volatile content, water content, and density of multi-component coatings, use the following procedures:

3.7.1 *Prepare about 100 ml of sample by mixing the components in a storage container, such as a glass jar with a screw top or a metal can with a cap. The storage container should be just large enough to hold the mixture. Combine the components (by weight or volume) in the ratio recommended by the manufacturer. Tightly close the container between additions and during mixing to prevent loss of volatile materials. However, most manufacturers mixing instructions are by volume. Because of possible error caused by expansion of the liquid when measuring the volume, it is recommended that the components be combined by weight. When weight is used to combine the components and the manufacturer's recommended ratio is by volume, the density must be determined by Section 3.4.*

3.7.2 *Immediately after mixing, take aliquots from this 100 ml sample for determination of the total volatile content, water content, volume solids, and density. To determine water content, follow Section 3.3. To determine density, follow Section 3.4. To determine volume solids content, follow Section 3.5. To determine total volatile content, use the apparatus and reagents described in*

ASTM D2369-81, Sections 3 and 4, respectively, and the following procedures:

- 3.7.2.1** *Weigh and record the weight of an aluminum foil weighing dish. Add 3 ± 1 ml of suitable solvent as specified in ASTM D2369-81 to the weighing dish. Using a syringe as specified in ASTM D2369-81, weigh to 1 mg, by difference, a sample of coating into the weighing dish. For coatings believed to have a volatile content less than 40 weight percent, a suitable size is 0.3 ± 0.10 g, but for coatings believed to have a volatile content greater than 40 weight percent a suitable size is 0.5 ± 0.10 g. Note: If the volatile content determined pursuant to Section 5 is not in the range corresponding to the sample size chosen repeat the test with the appropriate sample size. Add the specimen dropwise, shaking (swirling) the dish to disperse the specimen completely in the solvent. If the material forms a lump that cannot be dispersed, discard the specimen and prepare a new one. Similarly, prepare a duplicate. The sample shall stand for 1 hour, but no more than 24 hours prior to being oven dried at $110^{\circ}\text{C} \pm 5^{\circ}\text{C}$ for 1 hour.*
- 3.7.2.2** *Heat the aluminum foil dishes containing the dispersed specimens in the forced draft oven for 60 minutes at $110 \pm 5^{\circ}\text{C}$. Caution - provide adequate ventilation, consistent with accepted laboratory practice, to prevent solvent vapors from accumulating to a dangerous level.*
- 3.7.2.3** *Remove the dishes from the oven, place immediately in a desiccator, cool to ambient temperature, and weight to within 1 mg.*
- 3.7.2.4** *Run analyses in pairs (duplicate sets) for each coating mixture until the criterion in Section 4.3 is met. Calculate W_v following Equation 24-1 and record the arithmetic average.*

4. Data Validation Procedures

4.1 Summary. The variety of coatings that may be subject to analysis makes it necessary to verify the ability of the analyst and the analytical procedures to obtain reproducible results for the coatings tested. This is done by running duplicate analyses on each sample tested and comparing results with the within-laboratory precision statements for each parameter. Because of the inherent increased imprecision in the determination of the VOC content of waterborne coatings as the weight percent water increases, measured parameters for waterborne coatings are modified by the appropriate confidence limits based on between-laboratory precision statements.

4.2 Analytical Precision Statements. The within-laboratory and between-laboratory precision statements are given below

	Within-laboratory	Between-laboratory
Volatile Matter Content, W_v	1.5% $\overline{W_v}$	4.7 % $\overline{W_v}$
Water Content, W_w	2.9% $\overline{W_w}$	7.5% $\overline{W_w}$
Density, D_c	0.001 kg/liter	0.002 kg/liter

4.3 Sample Analysis Criteria. For W_v and W_w , run duplicate analyses until the difference between the two values in a set is less than or equal to the within-laboratory precision statement for that parameter. For D_c run duplicate analyses until each value in a set deviates from the mean of the set by no more than the within-laboratory precision statement. After several attempts, if it is concluded that the ASTM procedures cannot be used for the specific coating with the established within-laboratory precision, the Administrator will assume responsibility for providing the necessary procedures for revising the method or precision statements upon written request to: Director, Emission Standards and Engineering Division, (MD-13) Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

4.4 Confidence Limit Calculations for Waterborne Coatings. Based on the between-laboratory precision statements, calculate confidence limits for waterborne coatings as follows:

- To calculate the lower confidence limit, subtract the appropriate between-laboratory precision value from the measured mean value for that parameter.
- To calculate the upper confidence limit, add the appropriate between-laboratory precision value to the measured mean value for that parameter.
- For W_v and D_c , use the lower confidence limits, and for W_w , use the upper confidence limit. Because V_s is calculated, there is no adjustment for the parameter.

5. Calculations

5.1 Nonaqueous Volatile Matter.

5.1.1 Solvent-borne Coatings.

$$W_o = W_v \quad \text{Eq. 24-2}$$

Where:

W_o = Weight fraction nonaqueous volatile matter, g/g.

5.1.2 Waterborne Coatings.

$$W_o = W_v - W_w \quad \text{Eq. 24-3}$$

5.1.3 Coatings Containing Exempt Solvents.

$$W_o = W_v - W_E - W_w \quad \text{Eq. 24-4}$$

5.2 Weight Fraction Solids.

$$W_s = 1 - W_v \quad \text{Eq. 24-5}$$

Where:

W_s = Weight solids, g/g.

SECTION 4

STANDARD OPERATING PROCEDURES FOR METHOD 24 ANALYSES

PRIMARY ASTM METHODS

EPA Method 24 calls for the determination of density by ASTM D1475-60 (Reapproved 1980), volatile content by ASTM D2369-81, and water content by either ASTM D3792-79 (gas chromatography) or ASTM D4017-81 (Karl Fischer titration) of coating samples taken by regulatory agency personnel. ASTM D4457-85 is considered the best guidance presently available to determine the exempt solvent content of coatings.

SAMPLE CHARACTERIZATION STEPS

General

It is essential to make use of all the characterization information that may be available on the sample to proceed expeditiously. If the MSDS forms are available with the samples (as they should be), it can be determined if a highly volatile solvent, such as a light petroleum ether, is present or if the sample consists of more than 70-75% volatile solvents. Otherwise, a phone call can be made to the sending agency to determine the approximate solvent composition expected. This helps to determine the amount of sample to be used in the volatile content analysis to obtain a good reading on the volatile content, using ASTM D2369-81.

Step 1

The first step to be taken with a sample is opening and examining it in the hood. Important points to note here include amount of sample relative to container size (full, almost full, 3/4 full, etc.), color, viscosity, and uniformity. If questions arise at this point because of a conflict of observation with included information, the sending agency must be contacted to determine the proper course of action.

Step 2

If specific exempt solvent assay is requested, then the preparation of aliquots of sample for the determination of the content of the solvent should begin right after the sample examination. The standard test method ASTM D4457-85 for determination of dichloromethane (methylene chloride) or 1,1,1-trichloroethane (methyl chloroform) is being considered for incorporation into EPA Method 24. If the exempt solvent assay is not run immediately these aliquots should be securely sealed and stored at -20 C until

the assay is performed. At any rate, during the performance of analytical procedures, ideally no interruptions should be allowed and sample containers should always be kept sealed except when they must be opened to take or transfer sample material. The results of assays for exempt solvents (and of the water assay to be done later in the procedure) will be subtracted from the total volatile content.

Step 3

The total volatile content will be determined using ASTM D2369-81. This should follow the previous step with minimal delay to ensure the best estimate of the total volatile content.

Step 4

The next step in the procedure should be the analysis for water content by either ASTM D3792-79 (gas chromatography) or ASTM D4017-81 (Karl Fischer titration). One of two conditions should exist before this step is included: either the sending agency specifically requests analysis for water content or the documentation accompanying the sample indicates the presence of water. Care is taken during all previous steps to prevent the coating sample from absorbing water. The total volatile content reported would be too high if the sample absorbed water in the lab.

Step 5

The density determination using ASTM D1475-60 (Reapproved 1980) is always done last because it entails use of a large quantity of sample and would provide the maximum opportunity for sample volatilization.

SOPs FOR REFERENCE METHOD 24 ANALYSES

The following five procedures have been adapted from the pertinent ASTM methods to provide additional detail as well as to provide step-by-step procedures to be followed in their use under EPA Method 24. The five procedures are presented in the following order:

- Determination of Percent Water Content in Coating Samples by Gas Chromatography (Adapted from ASTM D3792-79)
- Determination of Water Content in Coatings by Karl Fischer Titration (Adapted from ASTM D4017-81)
- Determination of Percent Volatile Content in Coating Samples (Adapted from ASTM D2369-81)

- Determination of Density of Paint, Varnish, Lacquer, and Related Products (Adapted from ASTM D1475-60)
- *Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph (Adapted from ASTM D4457-85)*

DETERMINATION OF PERCENT WATER CONTENT IN COATING SAMPLES BY GAS CHROMATOGRAPHY (Adapted from ASTM D3792-79)

METHOD: The percent water content is determined by direct injection into a gas chromatograph.

EQUIPMENT:

I. Glassware

- A. A bottle of 50 ml capacity with a cap having an inert liner - one.
- B. 20 ml scintillation vials with teflon inverted cone cap seals - three.
- C. 10 ml serum bottles - six + four per sample.
 - 1. Teflon coated septa - six + four per sample.
 - 2. Aluminum caps - six + four per sample.

II. Syringes and pipettes

- A. 10 ml disposable syringe with needle - one.
- B. 5 ml disposable syringe with needle - two.
- C. A 5 ml pipetting device with one disposable tip.
- D. A 200 μ l Eppendorf pipettor with three disposable tips.
- E. Transfer pipette (5 3/4" Pasteur type) - five per sample.
- F. A 10 μ l syringe with needle.

III. Chemicals

- A. Deionized water (H_2O).
- B. Anhydrous N,N-Dimethylformamide (DMF).
- C. Anhydrous 2-propanol (i-PrOH).
- D. Anhydrous n-propanol (n-PrOH).

- E. High purity, dry nitrogen (N_2).
- IV. Miscellaneous
 - A. Rubber tubing - 18 inches.
 - B. Bottle cap crimper.
 - C. Pressure regulator for N_2 tank.
- V. Analytical balance - Range 0-200 grams, Reproducibility: ± 0.1 mg
- VI. Gas Chromatograph (GC) - e.g., HP 5890 A
 - A. Thermal conductivity detector.
 - B. Porapak Q column - 10 ft.
- VII. Integrator - e.g., HP 3357 LAS or HP 3392 A.

Note: Anhydrous solvents in packaging similar to the Sure/Seal Packaging System employed by the Aldrich Chemical Company, Inc. allow storing and dispensing of the solvent without exposure to atmospheric moisture. This procedure describes using reagents packaged in that manner, but the steps described can cause deterioration of the septa and exposure of the solvent to atmospheric moisture. An alternative procedure would be used in a high humidity environment or to ensure the transfer of solvents as free of moisture as possible.

PROCEDURE:

- I. General Preparation
 - A. Assemble equipment needed.
 - B. Fill a 20 ml scintillation vial with deionized water, cap it, label the vial " H_2O ."
 - C. Label a 10 ml syringe with needle and the 50 ml bottle "DMF". One 5 ml syringe with needle and a 20 ml scintillation vial should be labeled "i-PrOH" and another 5 ml syringe with needle and 20 ml scintillation vial should be labeled "n-PrOH".

- D. The bottles containing anhydrous DMF, anhydrous i-PrOH and anhydrous n-PrOH can be slightly pressurized relative to the surrounding atmosphere with high purity, dry N₂ to facilitate the withdrawal of material.
1. Attach rubber tubing to N₂ supply manifold and close the other outlets.
 2. Turn on the N₂ to a very gentle flow (at 3-5 psig).
 3. Pressurize the DMF bottle while wearing gloves, remove the needle from the DMF syringe and insert the needle base in the open end of the tubing. (TAKE GREAT CARE to hold the needle in the tube firmly or it will be released at this point like a projectile.)
 4. Insert the needle in the septum of the DMF bottle and invert the bottle.
 5. When the bubbles decrease, right the bottle and remove the needle.
 6. Replace the needle on the DMF syringe.
 7. Repeat the procedure for i-PrOH and n-PrOH using the appropriate needle if needed.
 8. Turn off the N₂ flow.
- E. Using the 10 ml syringe labelled "DMF," withdraw the approximate amount of DMF needed (2 ml per serum bottle used in screening and analysis). Transfer the DMF to the labeled 50 ml bottle and cap.

II. Preparation of Screening Samples

- A. Label the 10 ml serum bottles needed for this step. One should be labeled "DMF," another "DMF + i-PrOH + n-PrOH." Additional bottles, one for each sample, should be labeled using the appropriate laboratory sample number.
- B. Pipet 2 ml DMF into the bottle labelled "DMF." Place septum (teflon side down) on top of the bottle, cover both with metal cap and crimp.
1. The action of the crimping tool should be gentle but firm.
 2. The cap should not move if sealed properly.

3. If it is loose, rotate the vial 1/4 turn and crimp again.
 4. Repeat until tightly sealed.
- C. Pipet 2 ml DMF, 200 μ l i-PrOH and 200 μ l n-PrOH into appropriately labeled bottle and cap as before.
- D. For each sample:
1. Shake can on paint shaker for 5 minutes.
 2. Pipet 2 ml DMF into bottle.
 3. Weigh to nearest 1 mg on balance.
 4. Remove the bottle to hood and add about 0.4 to 0.6 grams of sample dropwise using a transfer pipette.
 - a. Add 10 drops of sample and reweigh.
 - b. Estimate how many additional drops of sample to add.
 - c. In the hood add the sample dropwise until the required amount is added.
 - d. Reweigh to verify the amount added.
 - e. Make note of the total number of drops of sample added and the weight increase.
 5. Cap as before.
 6. Shake vigorously.

III. Screen Samples

- A. Use the DMF as the syringe rinse between every injection.
- B. Flush a 10 μ l syringe with the pure DMF from its labelled bottle five times. Dispose of the waste into a 20 ml scintillation vial set aside for waste DMF.
- C. Insert needle into DMF bottle all the way to the liquid level and repeatedly fill and empty the syringe to expel air. Raise the needle stopping in the

air space above the liquid. Pull the plunger to the 1 μ l mark drawing in air.

- D. Lower the needle into the liquid to be injected and pull the plunger to the 2 μ l mark. Raise the needle out of the liquid and advance the plunger to the 4 μ l mark. Verify the loading of exactly 1 μ l of liquid into the syringe before removal from the bottle.
- E. When it has been verified that the volume is accurate, remove the needle and syringe from the bottle.
- F. Using the GC conditions outlined in Section IX of this procedure, inject the contents of the syringe into the GC.
- G. Hit the start buttons on the GC and the integrator.
- H. Rinse the syringe with DMF at least five times disposing of the waste as before.
- I. Repeat steps A through H for the DMF + i-PrOH + n-PrOH solution and the sample solutions.
- J. The following information should be noted for each sample:
 - 1. The presence of solids which made filling the syringe difficult and what steps had to be used to fill the syringe. Options include the following:
 - a. Allowing the solids to settle, insert the needle into the air space. Advance the plunger to the 1 μ l mark drawing in air and then carefully invert the sample and load the sample.
 - b. Centrifugation using a Dynac tabletop centrifuge (or comparable equipment) at 70% maximum speed for five minutes. The samples are in long narrow tubes with screw caps. After centrifugation, the supernatant is transferred to a small bottle and then capped.
 - c. Filtration, if used, is a last resort. Cleaning the filter in any quantitatively accurate way is difficult.
 - 2. Approximate water content. For samples with little or no water, 0.6 g of material can be used later when preparing for analysis.

Those with enough water to overwhelm the detector should be prepared using 0.3 g, 0.2 g or 0.1 g as necessary.

3. Look for potential interference with i-PrOH elution. If the sample contains i-PrOH or peaks that would interfere with its quantification, select an alternative internal standard. Examine the elution peak of n-PrOH. If its elution position is free of interference, use it instead. In extreme cases ethanol may be used.

IV. Prepare Internal Standard

- A. Make the internal standard selection based on the screening results.
- B. Since in most cases either i-PrOH or n-PrOH will be satisfactory, using the labelled syringe withdraw the approximate amount of internal standard needed (1 ml + 0.75 ml per sample).

V. Prepare Blanks

- A. Label one 10 ml serum bottle B-1 and a second one B-2.
- B. Add 2.0 ml DMF with the appropriate pipettor to B-1.
- C. Weigh the bottle, using gloves or tissue when handling to prevent finger prints. Record the weight to the nearest 0.1 mg.
- D. Using the Eppendorf pipettor add 200 μ l + 5 drops of the selected internal standard.
- E. Weigh and record as before.
- F. Seal well and shake to mix.
- G. Repeat steps B through F using B-2.

VI. Prepare References

- A. Label one 10 ml serum bottle R-1 and a second one R-2.
- B. Follow steps B through E of the blank preparation procedure described above using the R-1 bottle.
- C. With the Eppendorf pipette and a clean tip add 200 μ l deionized H₂O.

- D. Weigh, record the weight, seal well and shake.
- E. Repeat steps B through D using R-2.

VII. Prepare Samples

- A. Label three 10 ml serum bottles for each sample with the unique sample identification number and add a different letter (A, B, or C) to each to make each bottle label unique.
- B. Mix paint or coating for five minutes on the paint shaker if it was not mixed recently.
- C. Follow steps B through E of the blank preparation procedure using the __A bottle.
- D. Modify the total weight of coating to be added using the data noted during the screening. The relationship of the number of drops to the weight noted during the sample screen preparation will help here. Add the sample now.
- E. Weigh, record the weight and cap the bottle immediately.
- F. Mix the sample vigorously.
- G. Repeat steps C through for the __B and __C bottles.
- H. Repeat steps B through G for the other samples.

VIII. Analyze Samples

- A. Use B-1 as the syringe rinse between every injection.
- B. Fill a 10 μ l syringe with B-1 five times, disposing of the liquid in the waste DMF vial.
- C. Draw in 1 μ l of B-1 as described earlier.
- D. Using the GC conditions outlined in section IX of this procedure, inject the contents of the syringe into the GC.
- E. Hit the start buttons on both the GC and the integrator.

- F. Rinse the syringe with B-1 five times, regardless of what was injected to clear the syringe of potential solid deposits.
- G. When the GC is ready for the next injection, rinse the syringe again with B-1 five times.
- H. Repeat steps C through G for each of the following: B-2, R-1, R-2, and the three bottles (A, B, and C) prepared for the paints or coatings being analyzed.

IX. GC Conditions

- A. Use a Hewlett Packard 5890 A gas chromatograph (or comparable equipment) with a thermal conductivity detector (TCD).
- B. Column.
 - 1. Packing Porapak Q
 - 2. Dimensions 10 ft-4 mm ID
 - 3. Column Material Glass-1/4" OD
- C. Use a Hewlett Packard 3357 Laboratory Automation System backed up by a Hewlett Packard 3392A integrator or equivalent equipment.
- D. GC parameters.
 - 1. Flows
 - a. Column 45 cc/min
 - b. Total (column + ref.): 112 cc/min
 - 2. Oven
 - a. Equilibrium time 0.25 min
 - b. Initial oven temperature 90°C
(for a new column) 70°C
 - c. Initial time 0.00 min
 - d. Rate 20°C/min

	e.	Final oven temperature	210°C
	f.	Final time	24.00 min
3.		Run length	30.00 min
4.		Signal 1	
	a.	Range	4
	b.	Zero	0.0
	c.	Attenuation	0
5.		Injector	
	a.	Injector A temperature	220°C
6.		Detector	
	a.	Detector A TCD	ON (+)
	b.	Detector temperature	240°C
7.		Purge ON	
E.		Integrator parameters.	
	1.	Zero	20
	2.	Attenuation 2	4
	3.	Chart speed	0.5 cm/min
	4.	Peak width	0.16
	5.	Threshold	5
	6.	Area reject	100
	7.	Time table	
	a.	INTG # 10	13.50 min

b. INTG # 10

18.80 min

F. To start GC turn on oven temperature and detector. When both lights are off, temperatures are at set points and the GC is ready.

G. When finished with analyses, turn off the detector and the oven.

H. GC maintenance.

1. Change the septum each day. Remember to turn off the detector and the oven while making the change.
2. Make sure that the nut holding the septum in place is tightly turned.
3. Make sure the TCD is turned off for the night.

X. Data

The following data should be recorded (I.S. is internal standard):

Sample Weights	Wt Vial+ DMF (g)	+ I.S. (g)	+ Water (g)	+ Sample (g)
B1				
B2				
R1				
R2				
<u> </u> A				
<u> </u> B				
<u> </u> C				

Where:

Wt Vial + DMF =	gross weight of vial and DMF solvent.
+ IS =	(Wt. Vial + DMF) + weight of internal standard added.
+ Water =	(+ IS) + weight of water added to reference sample R1 and R2.
+ Sample =	(+ IS) + weight of paint or coating added to each of A, B, or C for analysis

Sample Areas:	Water Area	I.S. Area	DMF Area
B1			
B2			
R1			
R2			
<u> </u> A			
<u> </u> B			
<u> </u> C			

Where:

Water Area	= G.C. area counts for water
I.S. Area	= G.C. area counts for the internal standard
DMF Area	= G.C. area counts for the DMF solvent

XI. Calculations

$A_{i,j}$ = Respective areas

$W_{i,j}$ = Respective weights

$$B_j = \frac{A_{water,j}}{A_{DMF,j}}$$

$$B_{Ave} = \frac{B_1 + B_2}{2}$$

$$A_{DMF-Ave} = \frac{A_{DMF,1} + A_{DMF,2}}{2}$$

$$B = B_{Ave} * A_{DMF-Ave}$$

$$R_j = \frac{W_{IS,j} * (A_{water,j} - B)}{W_{water,j} * A_{IS,j}}$$

$$R_{Ave} = \frac{R_1 + R_2}{2}$$

$$\% \text{ Water} = \frac{(A_{water} - B) * W_{IS} * 100}{A_{IS} * W_{Paint} * R_{Ave}}$$

Where:

i = Chemical compound

j = Blank or reference standard number (1 or 2)

B = area of the water peak in the blank

R = Response factor of water

Calculations are best performed by computer on a spreadsheet in conjunction with an automated data acquisition system for analytical input from the gas chromatograph system.

XII. Notes

- A. Whenever a coating sample contains more than 40% H₂O, a new sample should be prepared using 0.4 g, 0.2 g or 0.1 g of coating.
- B. If some compound elutes late and interferes with subsequent runs, increase the Final Time of the chromatograph run sufficiently to elute the substance prior to the start of the next run. A Final Time in the range of 25 minutes is usually sufficient to purge the column.

DETERMINATION OF WATER CONTENT IN COATINGS BY KARL FISCHER TITRATION
(Adapted from ASTM D 4017-81)

METHOD: The water content of coating materials is determined by dissolving the sample in a suitable solvent and titrating it directly with standardized Karl Fischer reagent to an electrometric end point.

EQUIPMENT:

I. Glassware/Labware

- A. Reagent bottle top volumetric dispensers for chemicals which must be maintained under anhydrous conditions.

II. Syringes

- A. A 100 μ l syringe with needle - one.
- B. A 10 ml disposable syringe without needle, but equipped with a cap - one.
- C. A 1 ml disposable syringe without needle, but equipped with a cap - one.

III. Chemicals

- A. Water, Type II reagent grade conforming to ASTM Specification D1193 is best. (This calls for the use of distilled water with a conductivity of less than 1.0 μ mho/cm at 25 °C.) Freshly deionized (DI) water may also be used.
- B. Karl Fischer Reagent (KFR), A solution which is available from suppliers of laboratory chemicals and which contains iodine, sulfur dioxide, and pyridine dissolved in ethylene glycol monomethyl ether. Methanol is not generally used because 1) it may not dissolve many common resins, 2) methanol reacts with some resins to produce water, and 3) methanol may participate in water-forming esterification reactions in the presence of certain mineral acids (for example, in the formation of acetals and ketals from reaction with aldehydes and ketones), respectively, or may participate in side reactions with certain amines and siloxanes.
- C. Pyridine, reagent grade. Available from suppliers of laboratory chemicals.

- D. 1-Ethylpiperidine, reagent grade. Available from suppliers of laboratory chemicals.

IV. Miscellaneous

- A. Safety Equipment. Auxiliary laboratory equipment should include provisions for hood ventilation of benchtop work space as well as ventilation of the general laboratory area, storage for chemical reagents, and storage for solvents and coatings and inks which present a flammability risk because of their volatile solvent content.

- V. Analytical Balance, Range: 0-200 grams, Reproducibility: ± 0.1 mg.

- VI. Karl Fischer Apparatus, manual or automatic, encompassed by the detailed description given in ASTM Standard E 203-75 Test Method for Water Using Karl Fischer Reagent. Apparatus should be equipped with a 20-25 ml buret with 0.1 ml divisions. A 1 ml microburet with 0.01 divisions may be obtained for analysis of samples containing less than 0.5% water by weight.

PROCEDURE:

I. General Preparation

A. Assemble equipment needed.

1. Check Karl Fischer Apparatus being used. Clean titration vessel if needed with fresh pyridine and discard waste liquid into a dedicated and sealed waste disposal container (e.g., a 5 gallon can with safety lid) which is stored in the hood. Perform preliminary equipment checkout steps (following equipment manufacturer's instructions).
2. Clean up work area, removing waste paper, solvent, chemical reagent, or used labware materials.
3. Follow manufacturer's maintenance and setup instructions for the Karl Fischer Apparatus being used.

B. Assemble Reagents.

1. Safety Precautions. The Karl Fischer Reagent (KFR) used in this procedure contains four toxic compounds, namely iodine, sulfur dioxide, pyridine, and ethylene glycol monomethyl ether. 1-ethylpiperidine used as a catalyst for the reagent should be

considered equally toxic to pyridine and therefore handled with the same care. All operations including dispensing of reagents should be carried out in a hood. Rubber gloves and a face shield should be worn when handling and transferring chemicals. Care must be exercised to avoid inhalation or skin contact.

2. MSDS (Material Safety Data Sheet) instructions. All reagents used should be supplied with MSDS forms which contain physical, chemical, and safety guideline/emergency information. The MSDS sheets should be available in the same laboratory area where the equipment is used. Particular attention should be paid to the recommended emergency procedures to be followed in the event of spillage or accidental inhalation or physical contact with the chemicals being used.
3. Maintain anhydrous conditions. Follow instructions regarding maintenance of purity and stability of reagent chemicals that are provided by laboratory chemical suppliers. Do not leave containers open or exposed to excessive sunlight or other extreme conditions of temperature, humidity, or in potential contact with other reactive materials. Use volumetric safety dispensers for reagent bottles which are available from laboratory equipment suppliers.

II. Standardize Karl Fischer Reagent

A. Charge Karl Fischer Apparatus with reagents.

1. Charge a clean, dry titration vessel (containing a magnetic stirring bar) with pyridine to a level sufficient to cover the electrode sensor tip plus 1 ml of 1-ethylpiperidine catalyst per 20 ml of pyridine. The 5% volumetric proportion of the catalyst yields the best titration performance. This step may be accomplished automatically by different apparatus but the net result should be the same as outlined above. The magnetic stirrer should be on at this time to provide mixing of the titration vessel solution. The stirring rate should be vigorous but the end point electrodes should remain fully submerged in the solution and excess bubble formation should be avoided.
2. Charge the Karl Fischer Reagent (KFR) dispensing buret with KFR to a point where an initial reading can be taken of the volumetric level. Follow manufacturer's instructions if automatic or digital dispensing provisions are included in the apparatus being used.

- B. Pretitrate pyridine/1-ethylpiperidine solution to the end point indicated by the equipment manufacturer by adding KFR from the dispensing buret to cause the end point to hold for at least 30 seconds. Record the volumetric level in the buret.
- C. Adjust the Karl Fischer apparatus for maximum electrode sensitivity and minimum titration rate. Follow manufacturer's guidelines.
- D. Weigh the water standard specimen. Fill the 100 μ l syringe with Type II reagent grade distilled water and weigh the syringe and water to the nearest 0.1 mg. Record the weight in grams to the fourth decimal place.
- E. Inject the water standard from the 100 μ l syringe into the titration vessel using the appropriate sample port in the Karl Fischer apparatus. If necessary, immediately replace the sample port stopper to reseal the titration vessel.
- F. Titrate the water standard to the end point using the KFR dispensing buret to cause the end point to hold for at least 30 seconds and record the KFR volumetric level.
- G. Weigh the empty syringe to the nearest 0.1 mg and record the weight in grams to the fourth decimal place.
- H. Calculate F (=Karl Fischer titre) in grams H₂O per ml of Karl Fischer Reagent used.
- I. Calculation formula:

$$F = J/P$$

Where:

F = KFR titre

J = water added, grams

P = KFR used, ml

The value of F should be calculated and recorded to four significant figures. Typical values of F are in the range of 0.004000 to 0.006000 grams/ml corresponding to a KFR titre volume, P of 12.5 to 8.33 ml, respectively for a 50 μ l (approximately 0.05 gram) water standard specimen or sample, J.

- G. Repeat the standardization until replicate values of F agree within 1%. Determine the mean of at least two such determinations. Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

III. Perform Screening Specimen Analysis

- A. Prepare the titration vessel and KFR buret as described in Steps II. A and II. B (except using the 25 ml buret for dispensing the KFR). Best results are obtained with fresh solvent solution, that is containing no previously titrated specimen in the vessel.
- B. Mix the coating or ink sample container thoroughly (e.g., in a bench scale paint shaker/mixer for a period of five minutes)
- C. Draw a sample of the coating or ink using a 1 ml or 10 ml syringe (with cap) applying the specimen size guidelines given in Table 1:

Expected Water, (%)	Approximate Specimen Weight (g)	Approximate Titrant Volume at 5 mg/ml titr (ml)
0.5 - 1.0	5	5 - 10
1 - 2	2 - 5	10 - 20
3 - 10	1 - 2	10 - 20
10 - 30	0.4 - 1.0	20 - 25
30 - 70	0.1 - 0.4	15 - 25
> 70	0.1	20

- D. Remove the syringe from the sample container, pull the plunger out a little further, wipe the excess material off the syringe, and replace the cap on the syringe tip. Weigh the filled syringe to the nearest 0.1 mg. Reseal the sample container.
- E. Inject the sample into the titration vessel containing the pretitrated pyridine solution (after removing the syringe cap) and immediately reseal the vessel, if necessary. A high stirring rate should be employed and at least 2 minutes (preferably 5 minutes) should be allowed for the sample to dissolve before starting the titration. Pull the plunger back out of the syringe and replace the cap.

F. Reweigh the emptied syringe to the nearest 0.1 mg and calculate the specimen weight by difference.

G. Calculation:

$$\% \text{ water} = (\text{milliliters KFR used} \times F \times 100) / (\text{grams of sample})$$

IV. Perform the Sample Analysis

A. Adjust the specimen size based on findings of the screening analysis and repeat the determination. The % water is determined by obtaining a duplicate set of measurements and taking the average of the two results, at a minimum.

B. If the calculation shows that 0.1 to 0.5 % water is present in the sample, repeat the procedure using a 1 gram specimen and a 1 ml microburet for KFR titration.

V. Notes

A. Accuracy-Repeatability/Reproducibility

1. Repeatability - Two results, each the mean of duplicate determinations, obtained by the same operator on different days should be considered suspect if they differ by more than 4.7 % relative.
2. Reproducibility - Two results, each the mean of duplicate determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than 15.0 % relative.

B. Interferences

1. The possibility of interfering side reactions or the formation of byproducts which prevent accurate determination of water content is always possible. This method has been developed to minimize those potential problems but if they are suspected, it should be reported.
2. It is essential to use care and follow precise procedures when dissolving and mixing the specimen samples to obtain a homogeneous and therefore representative sample of the coating or ink.

3. All reagents used should be less than one year old and from a reliable laboratory reagent supplier. Contamination of reagents and solutions may cause significant reproducibility problems.

C. Maintenance

1. Contamination of the KFR burets, the reagent reservoir glassware, the titration vessel, and the coating of the sensing electrodes are all potential problems to inspect for and to prevent by performing periodic cleaning.
2. Clean the titration vessel by rinsing with fresh pyridine. Do not use methanol or other solvents.
3. Maintain anhydrous conditions (dryness) in the titration vessel by checking that drying tubes are in good condition and are tightly connected. Replace desiccant when indicator color changes through half the tube.
4. Follow manufacturer's guidelines regarding electrode performance response and cleaning.

D. Disposal of Waste

1. A separate waste container, such as a 5 gallon solvent can with lid should be maintained for spent or used reagents resulting from the use and cleaning of the titration vessel. This should be emptied for periodic disposal as a hazardous laboratory waste by a reputable disposal organization.

DETERMINATION OF PERCENT VOLATILE CONTENT IN COATING SAMPLES (Adapted from ASTM D2369-81)

METHOD: The percent volatile content (including water) as a weight fraction is determined by measuring the weight loss of a known sample quantity, which has been heated for one hour (60 minutes) at 110°C in a forced-draft oven.

EQUIPMENT:

- I. Glassware
 - A. Bottles of 50 ml capacity with a cap having an inert liner - two.
- II. Syringes and Pipets
 - A. 5 ml disposable syringes without needle - one per sample.
 - B. A 10 ml pipette - one per sample.
- III. Chemicals
 - A. Deionized water (H₂O).
 - B. Toluene.
- IV. Miscellaneous
 - A. Aluminum foil weighing dishes - three per sample.
- V. Analytical balance - Range: 0-200 grams, Reproducibility: ±0.1 mg
- VI. Vacuum Oven and Vacuum Pump
- VII. Desiccator

PROCEDURE:

- I. General Preparation
 - A. Assemble equipment needed.
 - B. Put toluene in one of the 50 ml bottles and deionized water in the other.

II. Preparation of Samples

- A. Inscribe an identification mark on each of three aluminum weighing dishes (e.g. A, B, C) for each coating. Remember to add an identifying mark to separate the coatings if more than one is under study.
- B. Preheat the pans in the vacuum oven for 30 minutes at 110°C.
- C. Place the dishes in a desiccator to cool to ambient temperature (about 15 minutes).
- D. Weigh the dishes and record the weight.
- E. For each coating:
 1. Shake can on paint shaker for 5 minutes.
 2. Add 3 ml \pm 1 ml of suitable solvent (toluene or water) to each of the three weighing dishes using the 10 ml pipettor.
 3. Using the information obtained from the screening of samples prior to determination of water content, estimate volatile content and proceed.
 4. Add to each weighing dish 0.6 ml of coating if it has a volatile content less than 50 weight % or 0.8 ml if it has a volatile content greater than 50 weight %.
 - a. Use a 5 ml disposable syringe.
 - b. Fill the syringe with coating.
 - c. Weigh the filled syringe to the nearest 0.1 mg and record the weight.
 - d. Add an aliquot of the sample to the first dish, reweigh the syringe and record the weight.
 - e. Add an aliquot of the sample to the second dish, reweigh the syringe and record the weight.
 - f. Repeat this for the third dish.

5. Heat the prepared weighing dishes in the vacuum oven for 60 minutes at $110 \pm 5^{\circ}\text{C}$ with the vacuum valve cracked open but the vent wide open (indicated vacuum barely detectable on vacuum gauge, corresponding to 0.1 to 1" Hg vacuum).
6. Remove the dishes from the oven and place them immediately in a desiccator, cool to ambient temperature about 15 minutes and weigh them to the nearest 0.1 mg.

III. Data

The following data is recorded:

Samples	Pan Wt. (g)	Initial Wt. Sample + Syr (g)	Final Wt. Sample + Syr. (g)	Final Wt. Pan + Sample (g)	Final Wt. Sample. (g)
A					
B					
C					

VI. Calculations

%VOC = Percent volatile matter in coating.

W_i = Weight of the i th item.

$$W_{\text{Sample}} = W_{\text{InitSample+Syr}} - W_{\text{FinSample+Syr}}$$

$$\% \text{VOC} = \frac{W_{\text{Sample}} + W_{\text{Pan}} - W_{\text{FinSample+Pan}}}{W_{\text{Sample}}} * 100$$

DETERMINATION OF DENSITY OF PAINT, VARNISH, LACQUER, AND RELATED PRODUCTS (Adapted from ASTM D1475-60 (Reapproved 1980))

METHOD: The density of the liquid at 25°C expressed in gm/ml and lbs/gal is determined by the following procedure. The accurately known absolute density of distilled (or deionized) water is used to calibrate the volume of a container. The same container is filled with sample liquid and weighed. All measurements are taken after the container and contents equilibrate at 25°C.

EQUIPMENT:

I. Glassware

- A. Container for boiling and storing distilled water.
- B. Pycnometer - three per sample.

II. Syringes and Pipettes

- A. A 25 ml pipette - three per sample.

III. Chemicals

- A. Deionized water (H₂O).

IV. Miscellaneous

- A. Constant temperature bath held at 25°C ±0.1°C.
- B. Desiccator.

V. Analytical Balance - Range: 0-200 grams, Reproducibility: ±0.1 mg

PROCEDURE:

I. General Preparation

- A. Assemble equipment needed.
- B. Freshly boil deionized water for use in the calibration step.

II. Determine Tare Weight of the Dry Pycnometers

- A. Clean and dry the pycnometers and bring each of them to a constant weight.
 - 1. Strong acid or strong base cleaners and nonresidual solvents may be used with glass containers.
 - 2. For maximum accuracy, continue rinsing, drying, and weighing until the difference between two successive weighing does not exceed 0.001% of the weight of the container (0.0003 g for a 30 g pycnometer).
 - 3. Fingerprints on the container will change the weight and must be avoided.
 - 4. Record the weight. This and all subsequent references to recording of information refer to the written account kept in the data books for environmental samples.

III. Calibration of Pycnometers

- A. Fill the pycnometers with the freshly boiled distilled water (or freshly boiled deionized water) at a temperature below 25°C.
- B. Immediately remove excess overflowed water or water held in depressions by wiping dry with absorbent material.
- C. Avoid occluding air bubbles in the container.
- D. Bring the container and contents to 25°C using the constant temperature bath.
- E. Remove the excess overflow by wiping carefully with absorbent material. Avoid wicking of water out of the orifice.
- F. Dry the outside of the pycnometers.
- G. Immediately weigh the filled pycnometers to the nearest 0.001% of its weight (0.0003 g for a 30 g pycnometer).
- H. Record the weight.

IV. Density of the Sample

A. For each coating:

1. Shake can on paint shaker for 5 minutes if that has not been done recently.

B. Repeat III using the sample instead of distilled water and using the 25 ml pipette to load the pycnometer.

V. Data

The following data is recorded:

Samples	Pyc #	Pyc Wt. (g)	Pyc + Sample Wt. (g)	Pyc Vol. (ml)
<u> </u> A				
<u> </u> B				
<u> </u> C				

VI. Calculations.

For the calibration:

$$V = \frac{(N - M)}{0.997072}$$

Obtain the mean of at least three determinations.

Where:

V = volume of the pycnometer, ml.

N = weight of the pycnometer and water, g.

M = weight of the dry pycnometer, g.

0.997072 = absolute density of water at 25°C, g/ml

For the density determination:

$$D_m = \frac{(W-w)}{V} \quad \text{and} \quad D = D_m * K$$

Where:

D_m = density, g/ml and D = density, lb/gal.

W = weight of the filled pycnometer, g.

w = weight of empty pycnometer, g.

V = volume determined above, ml.

$K = 8.345404$

DETERMINATION OF DICHLOROMETHANE AND 1,1,1-TRICHLOROETHANE IN PAINTS AND COATINGS BY DIRECT INJECTION INTO A GAS CHROMATOGRAPH (Adapted from ASTM D4457-85)

METHOD: The percent dichloromethane and 1,1,1-trichloroethane content of coating material is determined by dissolving the sample in a suitable solvent and injecting it directly into a gas chromatograph. An internal standard is added to the sample in a known quantity before chromatography for calibration.

EQUIPMENT:

I. Glassware/Labware

- A. Reagent dispensing buret, 100 ml capacity - one.
- B. 20 ml scintillation vials with teflon inverted cone cap seals - five per sample.
- C. 25 ml vials capable of being septum sealed - six + four per sample.
 - 1. Teflon coated septa - six + four per sample.
 - 2. Aluminum caps - six + four per sample.

II. Syringes and pipettes

- A. 20 ml disposable syringes with needle - two.
- B. 10 ml disposable syringes with needle - six.
- C. 10 ml Eppendorf or equivalent volumetric pipettors with eight disposable tips - one.
- D. Transfer pipettes for dropwise addition of samples.
- E. A 10 μ l syringe with needle.

III. Chemicals

- A. Anhydrous N,N-Dimethylformamide (DMF), reagent grade.

- B. Anhydrous 1-propanol (or 1-PrOH, n-propanol), gas chromatography spectrophotometric grade.
- C. Anhydrous 2-propanol (or 2-PrOH, isopropanol), gas chromatography spectrophotometric grade.
- D. 1,1,1 - Trichloroethane (or TCE, methyl chloroform), reagent grade (see E).
- E. Dichloromethane (or DCE, methylene chloride), reagent grade (see E).
- F. Halogenated hydrocarbon stabilizers - Commercial grades of TCE and DCE contain stabilizers. Obtain the same solvent used in the coating or find the type and quantity of stabilizer used and add it to the pure solvent.
- G. Carrier gas, Nitrogen (N_2) of 99.995% or higher purity. High purity Helium may also be used.

IV. Miscellaneous

- A. Rubber tubing - 18 inches.
- B. Bottle cap crimper.
- C. Safety Equipment. Auxiliary laboratory equipment should include provisions for hood ventilation of benchtop work space as well as ventilation of the general laboratory area, storage for chemical reagents, and storage for solvents and coatings and inks which present a flammability risk because of their volatile solvent content.

V. Analytical Balance, Range: 0-200 grams, Reproducibility: ± 0.1 mg.

VI. Gas Chromatograph (GC) - e.g., HP 5890 A

- A. Thermal conductivity detector.
- B. Porapak column - 4 ft.

PROCEDURE:

I. General Preparation

- A. Assemble equipment needed.

1. Clean up work area, removing waste paper, solvent, chemical reagent, or used labware materials.
- B. Assemble reagents.
1. Safety Precautions. All operations including dispensing of reagents should be carried out in a hood. Rubber gloves and a face shield should be worn when handling and transferring chemicals. Care must be exercised to avoid inhalation or skin contact.
 2. MSDS (Material Safety Data Sheet) instructions. All reagents used should be supplied with MSDS forms which contain physical, chemical, and safety guideline/ emergency information. The MSDS sheets should be available in the same laboratory area where the equipment is used. Particular attention should be paid to the recommended emergency procedures to be followed in the event of spillage or accidental inhalation or physical contact with the chemicals being used.
 3. Maintain anhydrous conditions. Follow instructions regarding maintenance of purity and stability of reagent chemicals that are provided by laboratory chemical suppliers. Do not leave containers open or exposed to excessive sunlight or other extreme conditions of temperature, humidity, or in potential contact with other reactive materials. Use volumetric safety dispensers for reagent bottles which are available from laboratory equipment suppliers.
- C. Fill a 20 ml scintillation vial with dichloromethane, cap it and label the vial "DCM." Fill a 20 ml scintillation vial with 1,1,1-trichloroethane, cap it and label it "TCE."
- D. One 20 ml syringe with needle and a 20 ml scintillation vial should be labeled "1-PrOH" and another 20 ml syringe with needle and 20 ml scintillation vial should be labeled "2-PrOH". Set aside one 20 ml scintillation vial, label it "Waste DMF," loosely cover it with a septum and cap, but do not seal it.
- E. If the bottles containing anhydrous DMF, anhydrous 1-PrOH and anhydrous 2-PrOH are not slightly pressurized relative to the surrounding atmosphere then that must be done now. (This is needed to facilitate the withdrawal of material.)

1. Attach rubber tubing to N₂ supply manifold and close the other outlets.
 2. Turn on the N₂ to a very gentle flow.
 3. To pressurize the DMF bottle, wearing gloves remove the needle from the DMF syringe and insert the needle base in the open end of the tubing. (TAKE GREAT CARE to hold the needle in the tube firmly or it will be released at this point like a projectile.)
 4. Insert the needle in the septum of the DMF bottle and invert the bottle.
 5. When the bubbles decrease, right the bottle and remove the needle.
 6. Replace the needle on the DMF syringe.
 7. Repeat the procedure for 1-PrOH and 2-PrOH using the appropriate needle if needed.
 8. Turn off the N₂ flow.
- F. Check that the 100 ml dispensing buret is mounted on the DMF reagent bottle and that sufficient DMF reagent is present to do the analysis (approximately 20 ml for each 25 ml vial used in screening and analysis).

II. Preparation of Screening Samples

- A. Label the 25 ml vials capable of being septum sealed that are needed for this step. One should be labeled "DMF," another "DMF + 1-PrOH + 2-PrOH." Additional vials, one for each sample, should be labeled using the appropriate laboratory sample number.
- B. Weigh the vial labeled "DMF" to 0.1 mg, dispense 17 ml DMF into the bottle and weigh the vial again to determine the amount of DMF added. Place septum-teflon side down-on top of the vial, cover both with metal cap and crimp.
 1. The action of the crimping tool should be gentle but firm.
 2. The cap should not move if sealed properly.
 3. If it is loose, rotate the vial turn and crimp again.

4. Repeat until tightly sealed.
- C. Dispense 17 ml DMF, then pipet 2 ml + 10 drops 1-PrOH and 2 ml + 10 drops 2-PrOH into appropriately labeled vial obtaining weights of each of the three components added to 0.1 mg and cap as before.
- D. For each screening sample:
 1. Shake can on paint shaker for 5 minutes.
 2. Dispense 17 ml DMF into the sample vial.
 3. Weigh to the nearest 1 mg on the analytical balance.
 4. Remove the bottle to hood and add about 4 ml of sample dropwise using a 10 ml disposable syringe.
 - a. Add 10 drops of sample using a transfer pipette and reweigh.
 - b. Estimate how many additional drops of sample to add to bring the total sample addition amount up to 5 g.
 - c. In the hood add the sample dropwise until the required amount is added.
 - d. Reweigh to verify the amount added.
 - e. Make note of the total number of drops of sample added and the weight increase.
 5. Cap as before.
 6. Shake vigorously.

III. Screen samples

- A. Use the DMF from the 25 ml septum sealed vial as the syringe rinse between every injection.
- B. Flush a 10 μ l syringe with the pure DMF from its labelled bottle five times. Dispose of the waste into a 20 ml scintillation vial set aside for waste DMF and cover loosely with a septum and cap.

- C. Insert needle into DMF vial but stop in the air space above the liquid. Pull the plunger to the 1 μ l mark drawing in air and then lower the needle into the liquid and pull the plunger to the 2 μ l mark. Raise the needle out of the liquid and advance the plunger to the 4 μ l mark. Verify the loading of exactly 1 μ l of liquid into the syringe before removal from the bottle.
- D. When it has been verified that the volume is accurate, remove the needle and syringe from the vial.
- E. Using the GC conditions outlined in the GC section of this procedure, inject the contents of the syringe into the GC.
- F. Hit the start buttons on the GC and the integrator.
- G. Rinse the syringe with DMF at least five times disposing of the waste as before.
- H. Repeat steps A through F for the DMF + 1-PrOH + 2-PrOH solution and the sample solutions. If there is any doubt of the elution times of 1-PrOH or 2-PrOH, the pure components can be injected into the gas chromatograph for positive determination.
- I. The following information should be noted for each sample:
 - 1. The presence of solids which made filling the syringe difficult and what steps had to be used to fill the syringe, including:
 - a. Allowing the solids to settle, insert the needle into the air space. Advance the plunger to the 1 μ l mark drawing in air and then carefully invert the sample and load the sample.
 - b. Centrifugation using a laboratory tabletop centrifuge (or comparable equipment) at 70% maximum speed for five minutes. The samples are in long narrow tubes with screw caps. After centrifugation, the supernatant is transferred to a small bottle and it is then capped.
 - c. Filtration if used is a last resort. Cleaning the filter in any quantitatively accurate way is difficult.
 - 2. Approximate exempt solvent content. For samples with little or no exempt solvent present, 5 g of material can be used later when preparing for analysis. Those with enough dichloromethane or

1,1,1-trichloroethane to overwhelm the detector should be prepared using 3 g, 2 g, or 1 g as necessary.

3. Look for potential interference with 1-PrOH elution. If the sample contains 1-PrOH or peaks that would interfere with its quantification, select an alternative internal standard. Examine the elution peak of 2-PrOH. If its elution position is free of interference, use it instead. In extreme cases, ethanol, other alcohols, esters, or hydrocarbons may be used.

IV. Prepare internal standard (IS)

- A. Make the internal standard selection based on the screening results.
- B. Since in most cases either 1-PrOH or 2-PrOH will be satisfactory, use the labeled syringe to withdraw the approximately 20 ml amount of internal standard needed (10 ml + 7.5 ml per sample) and charge it to the labeled 20 ml scintillation vial.

V. Prepare Blanks

- A. Label one 25 ml vial B-1 and a second one B-2.
- B. Add 17 ml DMF from the reagent dispenser to B-1.
- C. Weigh the bottle, using gloves or tissue when handling to prevent finger prints. Record the weight to five decimal places.
- D. Using the Eppendorf (or equivalent) pipettor add 2.5 ml of the selected internal standard.
- E. Weigh and record as before.
- F. Seal well and shake to mix.
- G. Repeat steps B through F using B-2.

VI. Prepare References

- A. Label one 25 ml vial R-1 and a second one R-2.
- B. Follow steps B through E of the blank preparation procedure using the R-1 bottle.

- C. With the Eppendorf (or equivalent) pipette and a clean tip add 2.7 ml of dichloromethane.
- D. Weigh and record the weight.
- E. With the Eppendorf (or equivalent) pipette and a clean tip add 2.7 ml of 1,1,1-trichloroethane.
- F. Weigh and record the weight.
- G. Seal well and shake.
- H. Repeat steps B through G using R-2.

VII. Prepare Samples

- A. Label three 25 ml vials for each sample with the unique sample identification number and add a different letter (A, B, or C) to each to make each bottle.
- B. Mix paint or coating for five minutes on the paint shaker if it was not mixed recently.
- C. Follow steps B through E of the blank preparation procedure using the __A bottle.
- D. Modify the total weight of coating to be added using the data noted during the screening. The relationship of the number of drops to the weight noted during the sample screen preparation will help here. Add the sample now using a fresh 10 ml disposable syringe.
- E. Weigh, record the weight and cap the bottle immediately.
- F. Mix the sample vigorously.
- G. Repeat steps C through F for the __B and __C bottles.
- H. Repeat steps B through G for the other samples.

VIII. Analyze Samples

- A. Use B-1 as the syringe rinse between every injection.

- B. Fill a 10 μ l syringe with B-1 five times disposing of the liquid in the waste DMF vial.
- C. Draw in 1 μ l of B-1 as described earlier.
- D. Using the GC conditions outlined in the GC section of this procedure, inject the contents of the syringe into the GC.
- E. Hit the start buttons on both the GC and the integrator.
- F. Rinse the syringe with B-1 five times regardless of what was injected to clear the syringe of potential solid deposits.
- G. When the GC is ready for the next injection, rinse the syringe again with B-1 five times.
- H. Repeat steps C through G for each of the following: B-2, R-1, R-2, and the three bottles (A, B, and C) prepared for the paints or coatings being analyzed.

IX. GC Conditions

- A. Use a Hewlett Packard 5890 A gas chromatograph (or comparable equipment) with a thermal conductivity detector (TCD).
- B. Column.
 1. Packing Porapak R
 2. Dimensions 4 ft-4 mm ID
 3. Column Material Glass-1/4" OD
- C. GC parameters.
 1. Flows
 - a. Column 45 cc/min
 - b. Total (column + ref.) 100 cc/min
 2. Oven
 - a. Equilibrium time 0.25 min

	b.	Initial oven temp. (for a new column)	90°C 70°C
	c.	Initial time	0.00 min
	d.	Rate 20°C/min	
	e.	Final oven temperature	210°C
	f.	Final time	24.00 min
3.		Run length	30.00 min
4.		Signal 1	
	a.	Range	4
	b.	Zero	30.0
	c.	Attenuation	0
5.		Injector	
	a.	Injector A temperature	220°C
6.		Detector	
	a.	Detector A TCD	ON (+)
	b.	Detector temperature	240°C
7.		Purge ON	
D.		Integrator parameters.	
	1.	Zero	20
	2.	Attenuation 2	4
	3.	Chart speed	0.5 cm/min
	4.	Peak width	0.16
	5.	Threshold	5

6. Area reject 100
7. Time table
 - a. INTG # 10 13.50 min.
 - b. INTG # 10 18.80 min.

E. To start GC turn on oven temperature and detector. When both lights are off, temperatures are at set points and the GC is ready.

F. When finished turn off the detector and the oven.

G. GC maintenance.

1. Change the septum each day. Remember to turn off the detector and the oven while making the change.
2. Make sure that the nut holding the septum in place is tightly turned.
3. Make sure the TCD is turned off for the night.

X. Data.

The following data should be recorded:

Sample Weights	Wt Vial + DMF (g)	+ I.S. (g)	+ dichloro-methane (g)	+ 1,1,1-trichloro-ethane (g)	+ Sample (g)
B1					
B2					
R1					
R2					
__ A					
__ B					
__ C					

Where:

Wt Vial + DMF = gross weight of vial and DMF solvent.
 + IS = (Wt Vial + DMF) + weight of internal standard added.
 + dichloromethane = (+ IS) + weight of dichloromethane added to the reference samples R1 and R2.
 + 1,1,1-trichloroethane = (+ dichloromethane) + weight of 1,1,1-trichloromethane added to reference samples R1 and R2.
 + Sample = (+ IS) + weight of paint or coating sample added to each of A, B, or C for analysis.

Sample Areas	Dichloromethane Area	1,1,1-trichloromethane Area	I.S. Area	DMF Area
B1				
B2				
R1				
R2				
<u> </u> A				
<u> </u> B				
<u> </u> C				

Where:

Dichloromethane Area = G.C. Area counts for dichloromethane.
 1,1,1-Trichloromethane Area = G.C. Area counts for 1,1,1-trichloromethane.
 IS Area = G.C. Area counts for the internal standard.
 DMF Area = G.C. Area counts for the DMF solvent.

XI. Calculations

A_{ij} = Respective areas

$W_{i,j}$ = Respective weights

$$B_j = \frac{A_{ESj}}{A_{DMFj}}$$

$$B_{Ave} = \frac{B_1 + B_2}{2}$$

$$A_{DMF-Ave} = \frac{A_{DMF,1} + A_{DMF,2}}{2}$$

$$B = B_{Ave} * A_{DMF-Ave}$$

$$R_j = \frac{W_{ISj} * (A_{ESj} - B)}{W_{ESj} * A_{ISj}}$$

$$R_{Ave} = \frac{R_1 + R_2}{2}$$

$$\%Exemptsolvent(ES) = \frac{(A_{ES} - B) * W_{IS} * 100}{A_{IS} * W_{IS} * R_{Ave}}$$

Where:

i = chemical compound.

j = blank or reference standard number (1 or 2).

B = area of the exempt solvent (either dichloromethane or (1,1,1-trichloroethane) in the blank.

R = Response factor for the exempt solvent (either dichloromethane or 1,1,1-trichloroethane).

Calculations are best performed by computer on a spreadsheet in conjunction with an automated data acquisition system for analytical input from the gas chromatograph system.

XII. Notes

- A. Whenever a coating sample contains more than 40% of either dichloromethane or 1,1,1-trichloroethane, a new sample should be prepared using 3 g, 2 g, or 1 g of coating.
- B. If some compound elutes late and interferes with subsequent runs, increase the Final Time sufficiently to elute the substance prior to the start of the next run. A Final Time in the range of 25 minutes is usually sufficient to purge the column.
- C. Accuracy-Repeatability/Reproducibility for 1,1,1-trichloroethane.
 - 1. Repeatability - Two results, each the mean of duplicate determinations, obtained by the same operator on different days should be considered suspect if they differ by more than 3.0% relative.
 - 2. Reproducibility - Two results, each the mean of duplicate determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than 8.1% relative.
- D. Accuracy-Repeatability/Reproducibility for Dichloromethane.
 - 1. Repeatability - Two results, each the mean of duplicate determinations, obtained by the same operator on different days should be considered suspect if they differ by more than 3.0% relative.
 - 2. Reproducibility - Two results, each the mean of duplicate determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than 17.9% relative.

E. Interferences.

1. The possibility of interfering side reactions or the formation of byproducts which may prevent accurate determination of dichloromethane and 1,1,1-trichloroethane content is always possible. This method has been developed to minimize those potential problems but if they are suspected, it should be reported.
2. It is essential to use care and follow precise procedures when dissolving and mixing the specimen samples to obtain a homogeneous and therefore representative sample of the coating or ink.
3. All reagents used should be less than one year old and from a reliable laboratory reagent supplier. Contamination of reagents and solutions may cause significant reproducibility problems.

F. Maintenance.

1. Contamination of the glassware/labware, syringes and pipettes, reagent bottles, and dispensers are all potential problems to inspect for and to prevent by performing periodic cleaning.
2. Maintain anhydrous conditions (dryness) in reagent vessels and glassware/labware by keeping seals and lids in place and tightly connected.
3. Follow manufacturer's guidelines regarding reagent bottle and syringe/pipettor/dispenser handling and cleaning.

G. Disposal of waste.

1. A separate waste container, such as a 5 gallon solvent can with lid should be maintained for spent or used reagents from use and cleaning of the titration vessel. This should be emptied for periodic disposal as a hazardous laboratory waste by a reputable disposal organization.

SECTION 5

REFERENCE METHOD 24A--DETERMINATION OF VOLATILE MATTER CONTENT AND DENSITY OF PRINTING INKS AND RELATED COATINGS

1. Applicability and Principle

- 1.1 Applicability. This method applies to the determination of the volatile organic compound (VOC) content and density of solvent-borne (solvent reducible) printing inks or related coatings.
- 1.2 Principle. Separate procedures are used to determine the VOC weight fraction and density of the coating and the density of the solvent in the coating. The VOC weight fraction is determined by measuring the weight loss of a known sample quantity which has been heated for a specified length of time at a specified temperature. The density of both the coating and solvent are measured by a standard procedure. From this information the VOC volume fraction is calculated.

2. Procedure

2.1 Weight Fraction VOC.

2.1.1 Apparatus.

- 2.1.1.1 Weighing Dishes. Aluminum foil, 58 mm in diameter by 18 mm high, with a flat bottom. There must be at least three weighing dishes per sample.
- 2.1.1.2 Disposable Syringe. 5 ml.
- 2.1.1.3 Analytical Balance. To measure to within 0.1 mg.
- 2.1.1.4 Oven. Vacuum oven capable of maintaining a temperature of $120 \pm 2^{\circ}\text{C}$ and an absolute pressure of 510 ± 51 mm Hg for 4 hours. Alternatively, a forced draft oven capable of maintaining a temperature of $120 \pm 2^{\circ}\text{C}$ for 24 hours.

- 2.1.2 Analysis. Shake or mix the sample thoroughly to assure that all the solids are completely suspended. Label and weigh to the nearest 0.1 mg a weighing dish and record this weight (M_{x1}).

Remove a sample of the coating using a 5-ml syringe without a needle. Weigh the syringe and sample to the nearest 0.1 mg and record this weight (M_{cY1}). Transfer 1 to 3 g of the sample to the tared weighing dish. Reweigh the syringe and sample to the nearest 0.1 mg and record this weight (M_{cY2}). Heat the weighing dish and sample in a vacuum oven at an absolute pressure of 510 ± 51 mm Hg and a temperature of $120 \pm 2^\circ\text{C}$ for 4 hours. Alternatively, heat the weighing dish and sample in a forced draft oven at a temperature of $120 \pm 2^\circ\text{C}$ for 24 hours. After the weighing dish has cooled, reweigh it to the nearest 0.1 mg and record the weight (M_{x2}). Repeat this procedure for a total of three determinations for each sample.

- 2.2 Coating Density. Determine the density of the ink or related coating according to the procedure outlined in ASTM D1475-60 (Reapproved 1980), (incorporated by reference - see §60.17).
- 2.3 Solvent Density. Determine the density of the solvent according to the procedure outlined in ASTM D1475-60 (Reapproved 1980). Make a total of three determinations for each coating. Report the density D_o as the arithmetic average of the three determinations.

3. Calculations

- 3.1 Weight Fraction VOC. Calculate the weight fraction volatile organic content W_o using the following equation:

$$W_o = \frac{M_{x1} + M_{cY1} - M_{cY2} - M_{x2}}{M_{cY1} - M_{cY2}} \quad \text{Eq. 24A-1}$$

Report the weight fraction VOC W_o as the arithmetic average of the three determinations.

- 3.2 Volume Fraction VOC. Calculate the volume fraction volatile organic content V_o using the following equation:

$$V_o = \frac{\overline{W_o} \overline{D_c}}{\overline{D_o}} \quad \text{Eq. 24A-2}$$

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SECTION 6

STANDARD OPERATING PROCEDURES FOR METHOD 24A ANALYSES

APPLICATION OF EPA METHOD 24A

EPA Method 24A is performed on publication rotogravure inks for New Source Performance Standard (NSPS) compliance. These inks are viscous, solvent-based formulations which frequently must be transferred from sample containers with small or large blade spatulas. Although not needed to measure weight fraction VOC, to determine the volume fraction VOC, it is necessary to have a separate sample of the ink solvent for density measurement. There are no dispersing agent which are presently recommended to prevent incorporation of solvent compounds into the hardened dry residue remaining after oven treatment performed for VOC weight percent measurement.

VOC DETERMINATION

The determination of the VOC weight fraction is otherwise clearly described in the method and SOP for Method 24 given in Section 4. No additional instructions are considered necessary.

DENSITY DETERMINATION

In the process of making ink density determinations by ASTM D1475-60 (Reapproved 1980), it is critical to carefully pack the heavy coating into the pycnometer using small and large blade spatulas without allowing air bubbles or void spaces to be formed. It is also important to thoroughly clean the outside of the pycnometer and carefully avoid weighing errors which can significantly affect the accuracy of the VOC weight fraction determination. Otherwise, SOP guidance for use of ASTM D1475-60 with Method 24, given in Section 4, is applicable for use with Method 24A as well.

SECTION 7

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(Please read Instructions on the reverse before completing)

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16. ABSTRACT

Standard procedures are presented in this report for the handling and physical/chemical characterization of coating and ink samples that require analysis by EPA Reference Methods 24 or 24A (RM 24/24A) as found in 40 CFR 60, Appendix A. For the purpose of developing consistency among analytical laboratories nationwide, it delineates the activities deemed proper and necessary to ensure that an accurate and precise measurement of coating or ink sample properties are made. If the activities are conducted as described, questions concerning the validity and reproducibility of analyses performed can be avoided.

This Standard Operating Procedure (SOP) covers all types of industrial coating and printing ink operations, regardless of the method of application of coating or ink, including, for example, dip, spray, roll, flow, electrostatic, or electro-deposition processes. Special cases involving use of exempt solvents dichloromethane (methylene chloride) and 1,1,1-trichloroethane (methyl chloroform) or multi-component mixture coating formulations are covered in accordance with most recent technical and regulatory thinking, however, this is not a regulatory but a technical procedure guideline document.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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